

# The Dielectric Properties of Insulating Materials

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This article discusses the variation of dielectric constant and dielectric loss in the radio and power frequency range with the object of giving a simple picture of the type of mechanism which is able to produce anomalous dispersion in this range of frequencies. Some of the general characteristics of anomalous dispersion can be demonstrated as well on a simple and arbitrary model of the structure of dielectrics as on the more complex ones which correspond more closely to the actual structure of dielectrics. Such a derivation is given here in order to indicate the significance of the different factors which occur in the formulæ which have been proposed to account for the variation of dielectric constant and dielectric loss with frequency. This enables a distinction to be made conveniently between the general characteristics which are shared by several types of dielectric polarization and the special characteristics which are peculiar to a restricted class of polarizations or to a particular kind of polarization.

## II. DIELECTRIC POLARIZABILITY AND ANOMALOUS DISPERSION

IN a previous paper<sup>1</sup> the general features of the dependence of dielectric constant on frequency were indicated schematically for the entire range extending from the frequencies used in power transmission to those of ultra-violet light. In the range of frequencies below the infra-red (that is, in the electrical range of frequencies) anomalous dispersion is the rule, normal dispersion not having been observed as yet, except for piezo-electric materials, whereas at high optical frequencies normal dispersion is the predominant feature. In the intermediate infra-red region it is not surprising to find a behavior which shows anomalous and normal dispersion in more nearly equal degrees of prominence.

It will be recalled that anomalous dispersion is the type of frequency-variation in which the dielectric constant decreases with increasing frequency, while normal dispersion is the reverse of this, the dielectric constant or refractive index increasing as the frequency increases. The use of the term *anomalous dispersion* to describe the dependence of dielectric constant on frequency in the radio and power frequency range is now widespread, and seems quite appropriate, for it brings out the point that the variation of dielectric constant with frequency in

<sup>1</sup> Murphy and Morgan, *B. S. T. J.*, 16, 493 (1937).

the radio and power range is in certain respects the same type of phenomenon as optical anomalous dispersion.

Anomalous dispersion plays a very important part in the behavior of dielectrics in the electrical range of frequencies. It is seldom possible to interpret a set of measurements of dielectric constant or other dielectric properties without encountering some manifestation of anomalous dispersion or of the other characteristic types of behavior which follow as corollaries of it.

The two catagories, polarizability and dispersion, include a great deal of the dielectric behavior of insulating materials. This paper will deal primarily with anomalous dispersion, but the theory of anomalous dispersion is not entirely separable from that of the polarizations of which it is an attribute, so it will be necessary to discuss at least briefly the nature of dielectric polarization.

#### *The Relation between Polarizability and Dielectric Constant*

For our purposes a dielectric may be thought of as an assemblage of *bound charges*, where this term is intended to include the electrons and positive cores in atoms and molecules, the ions held at lattice points in ionic crystals and, in general, any assemblage of charged particles which are so bound together that they are not able to drift from one electrode to the other under the action of an applied electric field of uniform intensity. Actual dielectrics, of course, also contain some conduction electrons or ions which are free to drift through the material and discharge at the electrodes, producing a direct current conductivity. This conductivity is small at ordinary temperatures in materials classified as dielectrics.

The positions of these charged particles may be considered to be determined by an equilibrium of forces. When an electric field is applied this equilibrium is disturbed and the bound charges are displaced to new positions of equilibrium; then when the applied field is removed they revert to their initial positions. In the equilibrium positions which the charges occupy when a constant electric field has been impressed on the dielectric they have a larger potential energy than in their initial positions. Moreover, they do not revert instantly to their initial positions, and when the retardation is due to friction some of the potential energy of the bound charges is dissipated as heat in the dielectric.

When an alternating voltage is applied to the dielectric, we may think of the bound charges as moving back and forth with certain amplitudes, a different amplitude for each different type of bound charge. When the applied electric field is of unit intensity, the sum of the product of

amplitude and charge extended over all of the *bound* charges in a unit volume of the material determines the *dielectric constant* of the material. The energy dissipated as heat by the motions of these bound charges in the applied electric field represents the *dielectric loss* per second, a quantity which is proportional to the a.-c. conductivity after the d.-c. conductivity has been subtracted from it. The imaginary part of the complex dielectric constant is proportional to the dielectric loss per cycle.

While the physical meaning of the dielectric constant and dielectric loss can be conveniently described, as above, in terms of the amplitudes and energy relationships of bound charges in their motions in an applied electric field, a more useful basis for the discussion is that provided by the concept of polarizability. In the present application the polarizability is equivalent to the product of charge and amplitude, but it has the advantage of being a quantity which is defined and discussed in the general theory of electricity as well as in that of dielectrics. The dielectric constant is then found to be related closely to the polarizabilities of the assemblages of charged particles which the dielectric contains.

The polarization of an assemblage of charges is a quantity defined in electrostatic theory as the vector sum

$$\mathbf{p} = \sum e_i \mathbf{s}_i, \quad (1)$$

where  $\mathbf{s}_i$  is the distance of the  $i^{\text{th}}$  charge,  $e_i$ , from a point chosen as origin, and the summation is extended over all of the charges in the assemblage, for which  $e_i$  is a typical charge. (If the assemblage has no net charge ( $\sum e_i = 0$ ), the origin may be arbitrarily located without affecting the value of  $\mathbf{p}$ .)

The polarization is a vector quantity. It can be written as the product of a scalar quantity  $p$ , which represents the magnitude or electric moment of the polarization and a unit vector  $\mathbf{p}_1$  which gives the direction of the polarization; thus  $\mathbf{p} = p\mathbf{p}_1$ . As it will not be necessary to distinguish between the properties of isotropic and anisotropic materials in this article the direction of the polarization need not be emphasized. The notation will therefore be simplified, in general, by using the magnitude or scalar part of such vector quantities as the polarization, the electric field intensity and the displacement of charged particles.

To illustrate the application of equation (1) let us consider a very simple configuration consisting of two charges  $+e$  and  $-e$  (see Fig. 1). The vector polarization of this configuration is  $\mathbf{p} = e(\mathbf{s}_1 - \mathbf{s}_2) = p\mathbf{p}_1$ , where  $p$  is the magnitude or electric moment of the polarization and

$\mathbf{p}_1$  is a unit vector in the direction of the vector  $(\mathbf{s}_1 - \mathbf{s}_2)$ . If now one of these charges is an electron ( $e = 4.77 \times 10^{-10}$  e.s.u.) and the other a unit positive charge and they are separated by a distance of the order of magnitude of atomic distances ( $10^{-8}$  cm.),  $p$  has the value  $4.77 \times 10^{-18}$  e.s.u., or 4.77 Debye units. The permanent electric moments of molecules seldom exceed a few Debye units.

Let us now apply the definition contained in equation (1) to a dielectric material. In the first place it indicates that if we know the effective positions of the electrons and other charged particles which

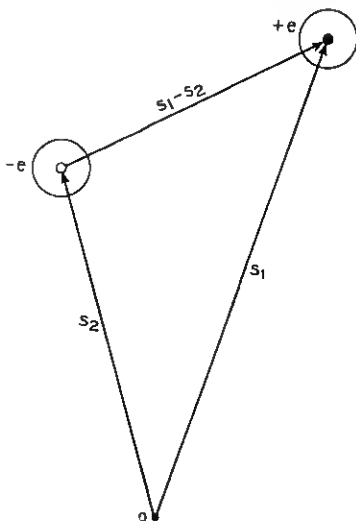


Fig. 1—The calculation of the polarization vector by the general method for a very simple configuration.

contribute to the structure of the material we can always, in principle, calculate the polarization of the body as a whole or any part of it. Actually the calculation of the polarization of a body as a whole or that of unit volume in it is in general a complicated matter involving statistical considerations, but there are special cases in which the result is rather obvious. For example, in a gas or liquid if all orientations of the molecules are equally probable in the absence of an applied field, the value obtained by taking the time-average of the summation indicated by (1) is zero. Equation (1) would also give the value zero when applied to all of the ions in a c.c. of a solution because any arbitrarily chosen small volume in the liquid would be as likely to contain a positive ion as a negative ion.

In some crystalline materials equation (1) gives the value zero because there is a suitable symmetry in the configuration of charged particles in the unit cell; for other solids equation (1) gives a finite value for the unit cell, but zero when applied to a volume of the material large enough to contain a great many crystallites with random orientations; however, there are some macroscopic crystals which have permanent polarizations. A solid material consisting of polar crystallites with random orientations is analogous, as far as equation (1) is concerned, to a liquid or gas containing polar molecules having random orientations; the polarization of the material as a whole is zero in either case.

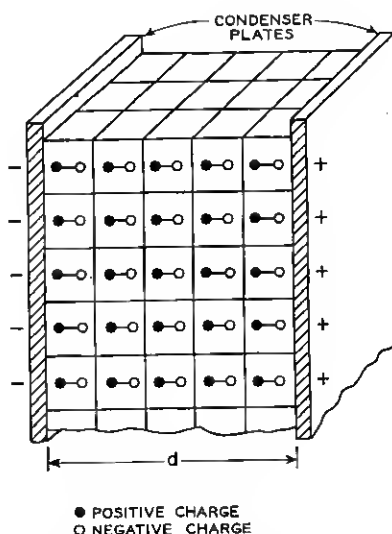


Fig. 2—A dielectric in a condenser. The circles joined by a bar represent "bound charges" of various kinds, including atoms and molecules.

Let us now consider a dielectric of any kind occupying the space between two plane, parallel condenser plates of great enough area and small enough separation that the electric field between the plates when they are charged may be considered to be directed normally to them (cf. Fig. 2). Consider the space between the plates of the condenser to be divided into small cubes of the same size, the purpose of this imaginary division of the dielectric being merely to obtain a representative specimen of the dielectric material. If the cube size is too small the instantaneous value of  $p$  obtained by applying equation (1) to all of the particles in a cube will vary appreciably from one cube to another;

but we can then increase the size of the cubes until  $p$  is the same for each cube to a close enough approximation. The polarization in each cube is then representative of that of the dielectric as a whole,<sup>2</sup> and by dividing  $\sum e_i s_i$  for a typical cube by the volume of the cube we obtain the *polarization per unit volume*, which for the present will be designated as  $P$ . This quantity is a statistical mean value involving a summation over a large number of particles; its value depends not only on the structure of the material but upon the effect of thermal motions on the mean positions and orientations of the molecules or other elementary particles in the material. One of the most interesting points in dielectric theory is the consideration—pointed out by Debye and at the basis of his theory of polar molecules—that for some types of structure the mean positions of the particles from which  $P$  is calculated are unaffected by changes in the amplitude of thermal motions while for another type of structure (consisting of polar molecules free to assume many or at least several orientations) an increase of temperature decreases  $P$ , because the randomness of the orientations of the polar molecules is increased.

For many materials  $P$  is zero when no electric field is applied, and assumes a finite value only when an electric field is applied, though as has been indicated, some crystalline materials have a finite value of  $P$  even in the absence of an applied electric field. In either case, however, the application of an electric field causes the bound charges within the dielectric to be shifted in general to new equilibrium positions, corresponding to the slight change in the system of forces acting upon them, and if the material did not have a polarization before the application of the field, it assumes one; if it did, it assumes a different value of  $P$ . The value of  $P$  when an electric field  $E$  is applied will be designated as  $P_E$ , and that when no field is applied by  $P_0$ . Then  $P_E - P_0$  is the polarization per unit volume induced by an applied field  $E$ . As the dielectric constant of a material depends upon the magnitude of the polarization induced in it by an applied field, and we are concerned here with dielectric constants, it will be desirable to simplify the notation by setting  $P_E - P_0 = P$ . This gives  $P$  a slightly different meaning than it had in the earlier part of the discussion, where it represented the total polarization per unit volume whatever its origin.

<sup>2</sup> A detailed consideration of the method of dividing a dielectric up into elementary volumes in order to compute the mean polarization encounters complications which need not be discussed here. A critical analysis of the method of computing the volume density of polarization of a dielectric is given by Mason and Weaver, "The Electromagnetic Field," Chicago (1929); Chapter III.

The relation between the applied electric field,  $E$ , and the polarization induced by it per unit volume is given by

$$P = \frac{\epsilon - 1}{4\pi} E \quad (2)$$

for isotropic materials. The constant  $(\epsilon - 1)/4\pi$  is the *susceptibility* of the dielectric in e.s.u., and  $\epsilon$  is the dielectric constant, which is defined as  $C/C_0$ , where  $C$  is the capacitance of the measuring condenser while it contains the dielectric and  $C_0$  is its capacitance when empty.

For some purposes there are advantages in considering the actual polarization, which is produced by a discontinuous distribution of charged particles, to be replaced by a vector point function which gives equivalent external effects. Then a vector  $\mathbf{P}$  may be considered to be associated with every point in the space occupied by the dielectric and the dielectric may be considered to have a continuous volume density of polarization,<sup>3</sup>  $\mathbf{P}$ . In non-isotropic bodies the polarization vector  $\mathbf{P}$  induced by an applied field  $\mathbf{E}$  is not always in the same direction as  $\mathbf{E}$ , but is assumed to be a linear vector function<sup>4</sup> of  $\mathbf{E}$  (involving, in the general case, six independent constants), where both  $\mathbf{E}$  and  $\mathbf{P}$  are vector point functions.

In deriving the relationship between the dielectric constant and the molecular structure of a material it cannot be assumed in general that the local field which is impressed upon the elementary particles in the dielectric is simply the field  $E$  which can be computed by dividing the applied voltage  $V$  by the distance between the plates of the condenser, the intensity of the field being assumed to be uniform. For there is an interaction between the molecules of the dielectric such that each molecule exerts a force on every other molecule. In the absence of an applied electric field these forces combine with other influences to create a distribution for which the polarization per unit volume has the value  $P_0$  (frequently zero, as has been mentioned). Then when a field is applied each element of volume in the dielectric is put into a polarized condition and in general the forces which it exerts upon the particles in other volume elements changes, because the charges in each volume element have been displaced to new positions. Consequently, the value assumed by  $P$  in a given cube of Fig. 2 will depend not only upon the direct action of the charges on the plates of the condenser—which determines the strength of the field  $E$ —but also

<sup>3</sup> Cf. Mason and Weaver, loc. cit. Chap. III.

<sup>4</sup> Cf. P. Debye, "Polar Molecules," Chemical Catalogue Co., New York (1929), pp. 32-35.

upon their indirect action through the polarization which they create in other elements of volume.

The contribution which the polarization of the dielectric makes to the force upon a charged particle in it has been calculated by Lorentz to be  $(4\pi/3)P$ , where  $P$  is the polarization per unit volume induced by the applied field. This calculation applies to an array of particles with cubic symmetry and to isotropic materials.<sup>6</sup> The *internal or local field*  $F$  is then given by

$$F = E + \frac{4\pi}{3} P. \quad (3)$$

$E$  may be thought of as the force which has its origin in the direct interaction between the charges on the plates of the condenser and the charges in the polarizable complex on which attention has been fixed (such as one of the cubes of Fig. 2), while the term  $(4\pi/3)P$  may be regarded as an indirect force coming from the other parts of the dielectric by virtue of their polarized state.

It is assumed in the theory of dielectrics that the structure of materials is such that  $P$  is a linear function of  $F$  (or a linear vector function in the case of anisotropic materials); then

$$P = kF, \quad (4)$$

where  $k$  is the polarizability per unit volume. It can be seen that

$$F = \frac{E}{1 - Ak}, \quad (4a)$$

where  $A = 4\pi/3$ , and consequently that the relation between the polarizability  $k$  and the susceptibility  $(\epsilon - 1)/4\pi$  ( $\equiv K$ ) is

$$K \equiv \frac{\epsilon - 1}{4\pi} = \frac{k}{1 - Ak}, \quad (4b)$$

whenever (3) is a valid expression for the internal field.

The susceptibility can be calculated without presupposing the validity of equation (3) for the internal field, *while the value of  $k$  depends upon whether (3) or some other expression gives the strength of the internal field in the dielectric.*

If  $L$  is the number of molecules per cubic centimeter,  $k/L$  ( $\equiv \alpha$ ) is the polarizability per molecule. This molecular constant  $\alpha$  is called the polarizability of the molecule. By multiplying  $\alpha$  by Avogadro's number  $N$ , we obtain the polarizability per mole of the dielectric:

<sup>6</sup> H. A. Lorentz, "The Theory of Electrons," p. 138, and Notes 54 and 55.



$N\alpha = Nk/L$ . And if  $m$  is the mass of a molecule,  $Nm = M$ , where  $M$  is the molecular weight, and  $Lm = \rho$ , where  $\rho$  is the density; so that

$$\frac{N}{L} = \frac{M}{\rho}$$

and the polarizability per mol may be written as  $Mk/\rho$ .

From equations (3) and (4) (or 4b) it can be shown that the polarizability is related to the dielectric constant by the familiar relation

$$k = \frac{3}{4\pi} \left[ \frac{\epsilon - 1}{\epsilon + 2} \right], \quad (5)$$

which however is only valid when (3) is valid—and for some materials (3) is apparently not valid.

For gases the term  $(4\pi/3)P$  in (3) is so small as compared with  $E$  that  $F$  is approximately equal to  $E$  and

$$k = K = \frac{\epsilon - 1}{4\pi}. \quad (6)$$

The polarizability and susceptibility are then equal. The physical reason for this is that the ratio of intermolecular space to the space occupied by molecules is much larger in a gas than in a solid or liquid and the direct force exerted by the charges on the condenser plates on a charged particle in the dielectric is then much greater than the indirect force which they exert through the polarization induced in other molecules.

It is customary to call the quantity  $(4\pi/3)k$  the volume polarization, and it is often denoted by the letter  $p$ . The volume polarization may be thought of as  $4\pi/3$  times the polarization induced in the dielectric per unit volume per unit applied field. The convenience of using  $(4\pi/3)k$  instead of  $k$  comes from the occurrence of the factor  $4\pi/3$  in the relation (5) between dielectric constant and polarizability.

On dividing equation (5) by the density we obtain a quantity which is called the mass polarization, as it is  $4\pi/3$  times the polarizability per gram:

$$\frac{1}{\rho} \left[ \frac{\epsilon - 1}{\epsilon + 2} \right] = \frac{4\pi}{3} \frac{k}{\rho}. \quad (7)$$

And on multiplying (7) by the molecular weight of the material we obtain

$$\frac{M}{\rho} \left[ \frac{\epsilon - 1}{\epsilon + 2} \right] = \frac{4\pi}{3} \cdot \frac{M}{\rho} \cdot k = \frac{4\pi}{3} \frac{kN}{L} = \frac{4\pi}{3} N\alpha. \quad (8)$$

The quantity  $(4\pi/3)N\alpha$  is the *molar polarization*,  $N\alpha$  being the polarizability per mole.<sup>6</sup>

Equation (8), and also (7), expresses the Clausius-Mosotti relation when  $\alpha$  is considered to be a constant characteristic of the individual molecule and independent of density. The function of  $\epsilon$  on the left-hand side of (8) is independent of density whenever  $\alpha$  is independent of density.

The following relation, analogous to that of Clausius and Mosotti but expressed in terms of the refractive index  $n$ , was derived by Lorentz and by Lorenz:

$$\frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha. \quad (8a)$$

The left-hand member of this equation is called the *molar refraction*. Equations (8) and (8a) are equivalent because of the general relation between refractive index and dielectric constant ( $n^2 = \epsilon$ ), but owing to the fact that refractive indices are measured at optical frequencies the molar refraction contains only the electronic part of the total molar polarization of the material. Subtracting the molar refraction from the total molar polarization, is one of the methods of determining the amount of polarization contributed by non-electronic polarizations.

It has been found that the Clausius-Mosotti relation is not equally satisfactory for all kinds of dielectric polarization. It gives good results when applied to electronic and atomic polarizations. For example, in an interesting paper on materials of high dielectric constant, Frank<sup>7</sup> has recently shown that the Clausius-Mosotti-Lorentz-Lorenz relationship aids materially in explaining the behavior of the dielectric constants of crystalline materials of high dielectric constant where the dielectric constant depends upon electronic polarizations. Where the polarizability of a molecule is the sum of the polarizabilities of the atoms of which it is composed it is to be expected that if the relation (5), or (8) or (8a) is valid the sum of the atomic polarizations would be equal to the molar polarization. Experimental agreement

<sup>6</sup> The polarizabilities of non-polar molecules and atoms are usually of the order of magnitude of  $10^{-24}$  c.c., and the molar polarizations of such substances, consequently, are of the order of magnitude of a few c.c., since the molar polarization is  $(4\pi/3) \times 6.06 \times 10^{23}$  times the polarizability of the individual molecule. The polarizability of a conducting sphere is equal to the cube of its radius. And, as atomic dimensions are of the order of magnitude of  $10^{-8}$  cm., it is evident that the polarizabilities of atoms tend to be of a similar order of magnitude to the polarizabilities which would be expected if they behaved as conducting spheres, though there are large differences in the ratio of polarizability to volume for different atoms. The molar polarizations of polar molecules are in general larger than those of similar non-polar molecules and may be a few hundred c.c. (Cf. P. Debye, "Polar Molecules," pp. 12-19.)

<sup>7</sup> F. C. Frank, *Trans. Faraday Society*, 23, (4), 513 (1937).

with this requirement has been found in optics where the refractive indices of molecules can be calculated approximately from the molar refraction (eq. 8a) obtained by adding the atomic refractions.

This additive property of electronic polarizations has been employed by Frank<sup>8</sup> to interpret the tendency of crystalline materials having high dielectric constants to be characterized by a high polarizability/volume ratio for the atoms or ions of which they are composed. This condition would tend to allow the largest number of highly polarizable particles to be concentrated in a given space, giving, on the additivity rule, a high molar polarization and a high dielectric constant.

On the other hand Wyman<sup>9</sup> has pointed out that the Clausius-Mosotti relation is not satisfactory when applied to *highly polar liquids*, such as water, and has found that for these substances it appears to be more satisfactory to consider that the polarization is related to the dielectric constant by the empirical relation

$$\frac{\epsilon + 1}{8.5} = \frac{4\pi}{3} k. \quad (9)$$

The calculation of the internal field by Lorentz, which provides the theoretical basis for equation (8), was made before the theory of polar molecules had been developed, but equation (8) has since been applied tentatively to polar molecules.<sup>10</sup> The problem of obtaining an improved relationship between polarizability and dielectric constant for materials having molecules with permanent electric moments has been studied in recent years by several investigators.<sup>11</sup> The calculation of the internal field usually involves the assumption that the effect of the molecules included in a small sphere surrounding the central molecule on which the force is being calculated is negligible on the average because of the random motions due to thermal agitation. On the supposition that such an assumption is not justified in a polar material because of the interactions of adjacent polar molecules, Onsager<sup>12</sup> has obtained a relation between polarizability and dielectric constant which for high dielectric constants is nearly the same as Wyman's empirical relation, equation (9). A comprehensive study of the effects of interaction between the dipoles of polar molecules has

<sup>8</sup> Loc. cit.

<sup>9</sup> Cf. Wyman, *Jour. Amer. Chem. Soc.*, 56, 539 (1934); 58, 1482 (1936).

<sup>10</sup> Cf. Debye, loc. cit., p. 13.

<sup>11</sup> Cf. Onsager, *Jour. Amer. Chem. Soc.*, 58, 1486 (1936); Van Arkel and Snoek, *Trans. Faraday Soc.*, 30, 707 (1934); Wyman, *Jour. Amer. Chem. Soc.*, 58, 1482 (1936); Van Vleck, *Jour. Chem. Physics*, 5, 320 (1937) and 5, 556 (1937).

<sup>12</sup> Loc. cit.

been made by Van Vleck by the methods of statistical mechanics. He obtains an expression which agrees to a second approximation with that obtained by Onsager. Thus it seems that for highly polar liquids the relations between polarization and dielectric constant developed by Onsager, Wyman and Van Vleck may be more satisfactory than the Clausius-Mosotti relationship, though for many other materials the Clausius-Mosotti relationship is apparently valid or approximately valid.

In deriving expressions for the dependence of dielectric constant on frequency later in this article the formulæ obtained will naturally depend upon which of the equations, (5), (6) or (9), is taken as the relationship between polarizability and dielectric constant. The alternative expressions will be listed.

### *Derivation of a Dispersion Formula*

The above-described relations between polarization and dielectric constant provide the means of obtaining expressions for the variation of dielectric constant with frequency when we have determined the dependence of polarizability on frequency. As our object is to exhibit the general features of anomalous dispersion shared by several particular types of polarization, it will be sufficient to derive dispersion formulæ containing constants the values of which are not specified, but which have a sufficiently obvious physical significance. The derivation given will parallel that of Lorentz in deriving a formula for optical dispersion,<sup>13</sup> and in fact is simply a special case of it in which certain terms are considered to be negligible by comparison with others.

An analogous procedure was used in one of the earliest attempts to explain anomalous dispersion in the electrical frequency range, the theory proposed by Drude<sup>14</sup> in 1898. This theory was based upon the hypothesis that anomalous dispersion in the electrical frequency range depends upon a mechanism similar to that to which optical dispersion was attributed, the difference being that the particles which produce anomalous dispersion in the electrical frequency range are so large that some of the terms in the optical dispersion formula can be neglected. The formulæ which Drude derived for electrical anomalous dispersion yield the same form of variation of dielectric constant with frequency as do the generally accepted theories of the present time, such as the Debye theory; the differences lie in the expressions given for the con-

<sup>13</sup> H. A. Lorentz, "The Theory of Electrons," Chapter IV. See also Korff and Breit, *Reviews of Modern Physics*, 4, 471 (1932), where a review of the classical theory of optical dispersion is given.

<sup>14</sup> P. Drude, *Ann. d. Physik*, 64, 131 (1898), "Zur Theorie der anomalien elektrischen Dispersion."

stants in the formulæ in terms of properties of the material. Another adaptation of optical dispersion theory to the explanation of dispersion in the electrical frequency range was proposed by Décombé<sup>15</sup> in 1912. He employed the Lorentz electron theory for the dispersion of light as a basis for the consideration that if the environment of some of the electrons in dielectrics is suitable their motions in an applied field could produce anomalous dispersion and dielectric loss in the electric frequency range. A similar simple and arbitrary assumption regarding the structure of dielectrics will also be employed here. However, it is not proposed as a theory of dielectric behavior but merely employed as a comparatively simple means of deriving and discussing relationships which can be demonstrated as well on a simple and arbitrary model as on the more complex ones which correspond more closely to the actual structure of dielectrics. The relation of the constants in the dispersion formulæ which will be derived here to the actual structure of dielectrics will only be indicated in a general qualitative way for the purpose of illustrating the physical nature of the processes involved; no attempt will be made to provide expressions for the dispersion constants in terms of other observable properties of the material.

In Fig. 2, let the applied potential be  $V$ , where  $V$  may vary in general in any way with the time, though in the present discussion it will be considered to vary sinusoidally with the time; the impressed field strength is then given by  $E = V/d$ . As in the more general discussion which preceded this, it will be assumed that the imaginary cells pictured in Fig. 2 contain large numbers of polarizable complexes consisting of positive and negative charges in equal numbers held in position by constitutive forces—the origin of which need not be specified for our present purposes—such that if they are displaced a distance  $s$  from their initial positions they will experience a force  $fs$ , where  $f$  is a constant, tending to restore them to their initial positions; and that while these charges are in motion as a result of the action of the impressed field they experience a frictional force  $r\dot{s}$ , where  $r$  is a constant and  $\dot{s}$  is the velocity in the direction of the impressed field; and, finally that their motion is also retarded by an inertia reaction  $m\ddot{s}$ , proportional to the mass  $m$  and the acceleration  $\ddot{s}$  of the particles.

The equation of motion for any typical charge  $e$  in a polarizable complex having the above-described specifications is

$$m\ddot{s} + r\dot{s} + fs = eF, \quad (10)$$

where  $F$  is given by equation (3) in materials to which the Lorentz calculation of the internal field applies, by  $F \cong E$  in the case of gases

<sup>15</sup> L. Décombé, *Journal de Physique*, (5), 3, 315 (1912).

and by other expressions—which in some cases may approximate either to  $F = E$  or to  $F = E + (4\pi/3)P$ —for still other materials. The quantities  $F$  and  $s$  are vectors, but for isotropic materials  $s$  is in the same direction as  $F$ .

If, following the method employed by Lorentz, we write an equation of the form (10) for each charged particle in a physically small volume  $\delta$  (such as the cubes of Fig. 2), multiply each equation by  $e$ , add the equations for all of the particles in  $\delta$ , and divide by the volume  $\delta$ , we obtain

$$m\ddot{P} + r\dot{P} + fP = ne^2F, \quad (11)$$

where  $P \equiv (1/\delta)\sum es$  and  $n$  is the number of charged particles characterized by the constants  $m$ ,  $r$  and  $f$  per unit volume. The volume  $\delta$  may be considered to be that of one of the cubes in Fig. 2. As indicated earlier it should contain a sufficient number of molecules to give a good mean value for  $P$ , the polarization per unit volume, but at the same time it should be small enough not to mask significant spatial variations in  $P$ .

When the impressed field  $E$  is varying sinusoidally with the time at the frequency  $\omega/2\pi$ , the local or internal field  $F$  tending to displace each charged particle in the dielectric will also vary sinusoidally with the time, though in general out of phase with  $E$ , if  $F$  is given by equation (3), and can be considered to be given by the real part of  $F_0e^{i\omega t}$ . Under these conditions

$$P = kF_0e^{i\omega t}$$

is a solution of equation (10) for the steady state provided that

$$k = \frac{ne^2}{(i r \omega - m \omega^2 + f)}. \quad (12)$$

$k$  is the polarizability per unit volume and is a complex quantity, since the term  $i r \omega$  in the denominator is an imaginary ( $i = \sqrt{-1}$ ).

Equations (10), (11) and (12) apply to a dielectric having a single type of polarization characterized by the constants  $f$ ,  $r$ ,  $m$ ,  $n$  and  $e$ . But in general an applied field induces several types of polarization simultaneously in a dielectric, and if we assume that it induces  $w$  types which are independent of each other, the total polarization per unit volume is given by

$$P = k_1F + k_2F + \cdots k_wF. \quad (13)$$

The total polarizability is then the sum of the individual polarizabilities, or

$$k = \sum_{j=1}^w k_j. \quad (14)$$

In this discussion it will be sufficient to consider that the different types of polarization designated by  $k_1, k_2 \dots k_w$  differ from one another only in having different sets of values for the constants of equation (12), designated by the subscripts 1, 2, 3  $\dots w$ ; for example, the character of the polarizability  $k_1$  is specified by the set of constants  $m_1, r_1, f_1$  and  $n_1$ .

In the first place it is evident that when the frequency of alternation of the voltage applied to the dielectric lies in the radio and power range it is possible to select any number of sets of values of  $m, r, f$  which will make the terms  $m\omega^2$  and  $r\omega$  negligible in comparison with  $f$  in the denominator of (12). Let  $m_1, r_1, f_1$  be an example of such a set of constants and let there be  $n_1$  particles per unit volume to which these constants apply. Then for this type of polarization equation (12) reduces to

$$k_1 = \frac{n_1 e^2}{f_1} \quad (15)$$

This type of polarization is independent of frequency and will be referred to as an instantaneous polarization or an optical polarization. The main representatives of the instantaneous or optical polarizations are the electronic and atomic polarizations, which experience dispersion in the visible and infra-red but which are independent of frequency in the electrical range, and the contribution of this polarizability to the dielectric constant is therefore frequently calculated from refractive index measurements.

A second type of polarization results if we assume that the dielectric we are considering contains a class of particles for which  $m\omega^2$  in equation (12) is negligible by comparison with  $r\omega$  and with  $f$ , but in which  $r\omega$  is of the same order of magnitude as  $f$  in the electrical range of frequencies. Let  $m_2, r_2, f_2$  be a typical member of this class, the number of such particles per unit volume of the dielectric being  $n_2$ . Then for this class of particles equation (12) becomes

$$k_2 = \frac{n_2 e^2}{(ir_2\omega + f_2)} \quad (16)$$

This expression represents the type of variation with frequency to which the name *anomalous dispersion* is given, and in the preceding paper the type of polarization which produces it was called an absorptive polarization.

It can readily be seen also that neglecting the  $m\ddot{s}$  term in (10) or the  $m\ddot{P}$  term in (11) leads to the same expression for  $k$ , i.e., equation (16), as does neglecting the  $m\omega^2$  term in the denominator of (12). So for any member,  $(r_2, f_2, n_2)$ , of the class of particles which produces

anomalous dispersion, equation (10) reduces to

$$r_2 \dot{s} + f_2 s = eF \quad (17)$$

and equation (11) becomes

$$r_2 \dot{P} + f_2 P = n_2 e^2 F. \quad (18)$$

Décombé's theory, which has been mentioned earlier, was based upon an equation equivalent in most respects to (18), while Drude's expressions for dispersion were obtained by a method equivalent to neglecting  $m\omega^2$  in (12).

Each term in equations (17) and (18) has an evident dynamical significance. Consequently, a physical picture of the essential nature of the anomalous dispersion process is given by equations (17) and (18) even though the values of constants  $r_2$ ,  $f_2$ ,  $n_2$  and  $e$  are not specified in terms of independently measurable properties of the dielectric. Thus the term  $f_2 s$  represents a restoring force tending to return the particles displaced by the impressed field to their initial positions, the constant  $f_2$  acting as a stiffness coefficient; the term  $r_2 \dot{s}$  acts as a frictional force,  $r$  being a measure of the friction experienced by, for example, a moving ion or a rotating polar molecule; and, finally,  $eF$  is the driving force tending to displace a particle of charge  $e$ . Evidently conditions which are sufficient to produce anomalous dispersion exist whenever the motion of charged particles in an applied field is sufficiently specified by considering the effects of a restoring force proportional to the displacement of the typical particle and of a frictional force proportional to the velocity of the particle in the direction of applied field, as in equation (17). Or, putting it in more general terms, we may say that anomalous dispersion occurs whenever the relation between the polarization per unit volume and the force due to the internal electric field is given by an equation which can be reduced to (18). However, the possibility that anomalous dispersion may also occur under conditions which cannot be described by equation (18) is not excluded by the considerations given here.

A third type of polarization which can be obtained by selecting suitable sets of values for the constants of equation (12) is that in which none of the terms in the denominator of (12) can be neglected in the electrical range of frequencies. Let  $k_3$  be the polarizability for this type of polarization which can then be represented by affixing the subscript 3 to the constants  $m$ ,  $r$ ,  $f$  and  $n$  of equation (12). This type of dispersion includes both the normal and the anomalous types but, as has already been indicated, in the radio and power ranges of fre-



quency examples of a dispersion of this kind have not as yet been observed in dielectrics which are not piezo-electric.<sup>16</sup> It follows then that dielectrics behave as though the inertia of the particles which contribute to dielectric polarization is small enough that the inertia reaction  $m\omega^2$  can be neglected in the electrical frequency range. This is an empirical result; the possibility of a polarization of the type  $k_3$  occurring in the electrical frequency range is not excluded by the general theory of dispersion. The higher the frequency of an impressed field the greater should be the likelihood of encountering the type of frequency-variation described by  $k_3$  (or equation (12)), because the prominence of the  $m\omega^2$  term increases with the square of the frequency.

The preceding discussion shows that we can write equation (14) in the form

$$k = k_i + k_a, \quad (19)$$

where  $k$  is the total polarizability,  $k_i$  is the sum of the instantaneous polarizabilities and  $k_a$  the sum of the absorptive polarizabilities, that is, of the polarizabilities which vary with frequency according to equation (16). If for simplicity we take the case in which the dielectric has only one representative of  $k_i$  and one of  $k_a$ , we obtain by substituting the values of  $k_i$  and  $k_a$  given respectively in (15) and (16),

$$k = \frac{n_1 e^2}{f_1} + \frac{n_2 e^2}{(ir_2 \omega + f_2)} \quad (20)$$

as an expression for the total polarizability.

Defining  $\tau'$  by  $\tau' \equiv r/f$ , and dropping the subscripts in (20) to make the notation simpler, we obtain

$$k = k_i + \frac{ne^2}{f} \left[ \frac{1}{1 + i\omega\tau'} \right], \quad (21)$$

which is the total polarizability per unit volume for a dielectric having two types of polarization, the one represented in (21) by the instantaneous polarizability  $k_i$  and the other by the absorptive polarizability

<sup>16</sup> Piezo-electric crystals such as quartz and Rochelle salt form exceptions, but for them dielectric polarization is coupled to macroscopic mechanical strains in the material and the mass reactance is due to the flexing or extension of the entire crystal. The dielectric constant of such a crystal as measured in almost any direction, shows an increase with increasing frequency, followed by anomalous dispersion. This is the behavior required by equation (12), or rather by an equation for the dielectric constant derivable from equation (12). This dispersion, however, depends upon the size and shape of the crystal, the nature of the electrodes and the manner of supporting the crystal during the measurements, and the exact interpretation of such measurements is a rather complex procedure. See, for example, W. F. Mason, *Proc. I. R. E.*, 23, 1252-1263 (1935).

specified by the second term on the right. The quantity  $\tau'$  is called the *relaxation-time*.

On multiplying the left-hand side of equation (21) by  $(4\pi/3)(M/\rho)$  and the right-hand side by  $(4\pi/3)(N/L)$  we obtain

$$\frac{4\pi}{3} \frac{Mk}{\rho} = \frac{4\pi}{3} N \left[ \frac{k_i}{L} + \frac{ne^2}{fL} \left( \frac{1}{1 + i\omega\tau'} \right) \right], \quad (22)$$

which is the molar polarization.

For dielectrics to which the Clausius-Mosotti relation applies, equation (8) shows that

$$\frac{4\pi}{3} \frac{Mk}{\rho} = \frac{M}{\rho} \frac{\epsilon - 1}{\epsilon + 2} \quad (22a)$$

and in fact the expression on the right-hand side of (22a) is frequently called the molar polarization. Reference to equation (6) shows, however, that for gases (22a) reduces to the simpler relation.

$$\frac{4\pi}{3} \frac{Mk}{\rho} = \frac{M}{\rho} \frac{(\epsilon - 1)}{3}. \quad (22b)$$

And for Wyman's relation between dielectric constant and polarizability, which has been discussed earlier, the molar polarization becomes

$$\frac{4\pi}{3} \frac{Mk}{\rho} = \frac{M}{\rho} \frac{\epsilon + 1}{8.5}. \quad (22c)$$

Equations (22a), (22b) and (22c) are not the only relations between dielectric constant and molar polarization which have been proposed, but they apparently cover moderately well many of the conditions met in practice. For the right-hand member of equation (22) can be substituted whichever of the three expressions (22a), (22b), (22c) seems the most suitable for the type of dielectric under investigation.

If in equation (21)  $\omega$  is set equal to zero we obtain the zero-frequency (or static) polarizability

$$k_0 = k_i + ne^2/f \quad (23)$$

and if  $\omega$  is set equal to infinity we obtain

$$k_\infty = k_i. \quad (24)$$

Subtraction gives

$$k_0 - k_\infty = ne^2/f. \quad (25)$$

Substituting (24) and (25) in (21) gives

$$k = k_\infty + \left( \frac{k_0 - k_\infty}{1 + i\omega\tau'} \right). \quad (26)$$

The constants  $ne^2/f$  and  $k_i$  are not present in (26), being replaced by two special values of the polarizability, the zero-frequency value and the infinite-frequency value. However, it is not the polarizability but the dielectric constant which is directly observed in measurements on dielectrics, so it is desirable to replace  $k_0$  and  $k_\infty$  by their equivalents in terms of the dielectric constant. But, as the earlier discussion has indicated, the relation between dielectric constant and polarizability is different for different types of dielectrics; three alternative expressions analogous to (22a), (22b) and (22c) will therefore be derived.

For materials to which equation (22a) (or the equivalent and simpler relation (5)) applies

$$k_0 - k_\infty = \frac{3}{4\pi} \left[ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] = \frac{9(\epsilon_0 - \epsilon_\infty)}{4\pi(\epsilon_0 + 2)(\epsilon_\infty + 2)}, \quad (27)$$

where  $\epsilon_0$  is the zero-frequency dielectric constant and  $\epsilon_\infty$  is the infinite-frequency dielectric constant. Then equation (26) can be replaced by

$$\frac{4\pi}{3} k = \frac{\epsilon_0 - 1}{\epsilon_\infty + 2} + \left[ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \frac{1}{1 + i\omega\tau'}. \quad (28)$$

By rationalizing and using the second expression given for  $k_0 - k_\infty$  in equation (27) we can write equation (28) in the alternative form

$$\begin{aligned} \frac{4\pi k}{3} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \left[ \frac{3(\epsilon_0 - \epsilon_\infty)}{(\epsilon_0 + 2)(\epsilon_\infty + 2)} \right] \cdot \frac{1}{1 + \omega^2\tau'^2} \\ - i \left[ \frac{3(\epsilon_0 - \epsilon_\infty)}{(\epsilon_0 + 2)(\epsilon_\infty + 2)} \right] \cdot \frac{\omega\tau'}{1 + \omega^2\tau'^2}. \end{aligned} \quad (29)$$

Equation (29) is the complex polarizability per unit volume multiplied by the factor  $4\pi/3$  and expressed in terms of observable values of the dielectric constant and the relaxation-time  $\tau'$ . The relaxation-time can also be expressed in terms of the reciprocal of a special value of the frequency; this permits all of the theoretical constants such as  $ne^2/f$  and  $\tau'$  to be replaced by certain special values of the dielectric constant and a critical value of the frequency.

A simpler expression for the polarizability is obtained in the case of gases, or whenever equation (6) gives the relation between polarizability and dielectric constant. Equation (26) then gives

$$\frac{4\pi k}{3} = \frac{1}{3} \left( \epsilon_\infty - 1 + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau'} \right). \quad (30)$$

And for materials to which the relation (cf. equation (9)) proposed by

Wyman applies the procedure followed above yields

$$\frac{4\pi k}{3} = \frac{1}{8.5} \left( \epsilon_{\infty} + 1 + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau'} \right). \quad (31)$$

On multiplying equations (29), (30) and (31) by  $M/\rho$  three alternative formulæ for the molar polarization of a dielectric having polarizations of the type specified by equation (21) are obtained; the constants in these formulæ include only special values ( $\epsilon_0$  and  $\epsilon_{\infty}$ ) of the dielectric constant and the relaxation-time, all of which can be obtained from dispersion curves.

The quantity  $k_0 - k_{\infty}$  is a constant of the material, which, as equation (26) shows, represents the largest value which the absorptive part of the total polarizability, i.e., the  $k_a$  term in (19), can have for a given material; it may be described as the zero-frequency or static value of the absorptive part of the polarizability. Evidence as to the nature of a polarization can be obtained by investigating experimentally the dependence of  $(k_0 - k_{\infty})/\rho$  on temperature; for example, if the polarization is due to the changes of orientation of polar molecules according to the Debye theory this quantity should increase linearly with the reciprocal of the absolute temperature. It is useful, therefore, to express  $(k_0 - k_{\infty})/\rho$  in terms of observable values of the dielectric constant so that it may be plotted against temperature. In this connection there is, however, the same complication which has appeared in other places in this discussion regarding the relation between dielectric constant and polarizability. The three relations which have been discussed here yield for  $(k_0 - k_{\infty})/\rho$  the following expressions:

$$(k_0 - k_{\infty})/\rho = \frac{3}{4\pi\rho} \left[ \frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \right] \text{ (Clausius-Mosotti)} \quad (32a)$$

$$= \frac{3}{4\pi\rho} \left( \frac{\epsilon_0 - \epsilon_{\infty}}{3} \right) \quad \text{(for gases)} \quad (32b)$$

$$= \frac{3}{4\pi\rho} \left( \frac{\epsilon_0 - \epsilon_{\infty}}{8.5} \right) \quad \text{(Wyman).} \quad (32c)$$

#### *The Complex Dielectric Constant*

As the dielectric constant ( $\epsilon$ ) is the quantity directly measured in experimental investigations it is desirable to determine how it should vary with frequency for the type of dielectric polarization described in equation (21) or (29). Solving equation (5) for  $\epsilon$  we obtain

$$\epsilon = \frac{1 + 8 \frac{\pi}{3} k}{1 - 4 \frac{\pi}{3} k}. \quad (33)$$

By substituting the expression for  $4(\pi/3)k$  given in equation (28) into (33) we obtain

$$\epsilon = \frac{\frac{\epsilon_0}{\epsilon_0 + 2} + i \frac{\epsilon_\infty}{\epsilon_\infty + 2} \omega \tau'}{\frac{1}{\epsilon_0 + 2} + i \frac{1}{\epsilon_\infty + 2} \omega \tau'} \quad (34)$$

or

$$\epsilon = \frac{\frac{\epsilon_0}{\epsilon_0 + 2} \left( 1 + i \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \cdot \frac{\epsilon_\infty}{\epsilon_0} \omega \tau' \right)}{\frac{1}{\epsilon_0 + 2} \left( 1 + i \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \omega \tau' \right)} \quad (34a)$$

Then, by setting

$$\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \tau' = \tau, \quad (35)$$

we obtain

$$\frac{\epsilon}{\epsilon_0} = \frac{\left( 1 + i \frac{\epsilon_\infty}{\epsilon_0} \omega \tau \right)}{1 + i \omega \tau} \quad (36)$$

and transforming this into polar form to facilitate division gives

$$\frac{\epsilon}{\epsilon_0} = \frac{\rho_1 e^{i\varphi_1}}{\rho_2 e^{i\varphi_2}} = \frac{\rho_1}{\rho_2} e^{i(\varphi_1 - \varphi_2)} = \frac{\rho_1}{\rho_2} \left[ \cos(\varphi_1 - \varphi_2) + i \sin(\varphi_1 - \varphi_2) \right], \quad (37)$$

where

$$\rho_1 = \left[ 1 + \left( \frac{\epsilon_\infty}{\epsilon_0} \right)^2 \omega^2 \tau^2 \right]^{\frac{1}{2}}, \quad \rho_2 = [1 + \omega^2 \tau^2]^{\frac{1}{2}},$$

$$\varphi_1 = \tan^{-1} \frac{\epsilon_\infty}{\epsilon_0} \omega \tau \quad \text{and} \quad \varphi_2 = \tan^{-1} \omega \tau.$$

Equation (37) then gives

$$\frac{\epsilon}{\epsilon_0} = \frac{1 + \frac{\epsilon_\infty}{\epsilon_0} \omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\left( \frac{\epsilon_\infty}{\epsilon_0} - 1 \right) \omega \tau}{1 + \omega^2 \tau^2} \quad (38)$$

or

$$\frac{\epsilon}{\epsilon_0} = \frac{\epsilon_\infty}{\epsilon_0} + \frac{1 - \frac{\epsilon_\infty}{\epsilon_0}}{1 + \omega^2 \tau^2} + \frac{i \left( \frac{\epsilon_\infty}{\epsilon_0} - 1 \right) \omega \tau}{1 + \omega^2 \tau^2}, \quad (38a)$$

from which we obtain

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} - \frac{i(\epsilon_0 - \epsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2}. \quad (39)$$

Equation (39) is the complex dielectric constant expressed in rectangular form for a dielectric having a polarizability (per unit volume) given by (21) and in which the internal field ( $F$ ) is such that the Clausius-Mosotti relation (equation (8)) applies.

For gases the derivation of the expression for the complex dielectric constant from that for the polarizability is simpler, though the same in principle, as the above. From (22*b*) or (6) we see that  $\epsilon = 1 + 4\pi k$ ; and on substituting (30) for  $4\pi k$  and rationalizing we obtain

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2 \tau'^2} - i \frac{(\epsilon_0 - \epsilon_{\infty}) \omega \tau'}{1 + \omega^2 \tau'^2}. \quad (40)$$

And when the relation between polarizability and dielectric constant is that proposed by Wyman, cf. (9) or (22*c*), we again obtain (40) on substituting (31) for  $(4\pi/3)k$  in (9) and rationalizing.

It will be noticed that the difference between (40) and (39) is that  $\tau'$  appears in the former and  $\tau$  in the latter,  $\tau$  being given by (35). This shows that the factor  $(\epsilon_0 + 2)/(\epsilon_{\infty} + 2)$  has its origin in the fact that for the conditions to which (39) applies  $F = E + (4\pi/3)P$ , while for the conditions to which (40) applies  $F = E$ , or is a linear function of  $E$ .  $\tau$  is the relaxation-time for the dielectric constant, while  $\tau'$  is the relaxation-time for the polarizable units in the material; when  $F = E$  these two relaxation-times are equal.

For materials of high dielectric constant the factor  $(\epsilon_0 + 2)/(\epsilon_{\infty} + 2)$  produces a considerable difference between  $\tau$  and  $\tau'$ ; for example, for water or ice  $\tau$  is about  $23\tau'$ . In a recent paper, R. H. Cole<sup>17</sup> has shown that when the volumes of certain polar molecules are calculated from  $\tau$  by means of Debye's expression for the relaxation-time better agreement with the volume estimated from van der Waals' equation is obtained when Onsager's relation between polarization and dielectric constant is used instead of the Clausius-Mosotti relation. In particular, for water the van der Waals coefficient gives  $13 \times 10^{-24}$  c.c. for the volume of the molecule, while  $\tau'$  gives  $0.5 \times 10^{-24}$  c.c. on the Clausius-Mosotti relation but  $12 \times 10^{-24}$  c.c. on the Onsager relation, and  $4 \times 10^{-24}$  c.c. for a modified Onsager relation. And if Wyman's relation is used,  $\tau = 23\tau'$ , and the volume should be 23 times that calculated on the basis of the Clausius-Mosotti relationship, or about  $11 \times 10^{-24}$  c.c.

Both equation (39) and equation (40) can be expressed in the form

$$\epsilon = \epsilon' - i\epsilon'', \quad (41)$$

<sup>17</sup> R. H. Cole, *Jour. Chem. Phys.*, 6, 385 (1938).

where

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2 \tau^2}, \quad (41a)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty})\omega\tau}{1 + \omega^2 \tau^2}, \quad (41b)$$

if  $\tau$  is considered to be given by

$$\tau = \frac{\epsilon_0 + 2}{\epsilon_{\infty} + 2} \tau',$$

when the complex dielectric constant is given by (39), that is when the Clausius-Mosotti relation applies, and by

$$\tau = \tau',$$

when the material is a gas, or when Wyman's relation between polarizability and dielectric constant applies.

The real part  $\epsilon'$  of the complex dielectric constant is usually referred to simply as the dielectric constant, while the imaginary part  $\epsilon''$  is frequently called the *loss factor*.<sup>18</sup> There are alternative ways of expressing the same property of the material; for example, the tangent of the loss angle,  $\epsilon''/\epsilon'$ , is frequently used instead of  $\epsilon''$ .

#### Comparison of Dispersion Formulae

Comparison of (39) or (41), (41a), (41b) with equation (69), page 97, of Debye's "Polar Molecules" shows that the equation for the complex dielectric constant derived here is identical with that of the Debye theory (in the present notation  $\tau'$  corresponds to  $\tau$  in Debye's book). This means that any characteristics which can be derived from equations (41), (41a), (41b) without specifying the values of the constants  $\epsilon_{\infty}$ ,  $\epsilon_0$  and  $\tau$  are common to at least two types of polarization, that is, to the polarization due to the effect of an applied field on the orientation of polar molecules according to the Debye theory, and to the polarization described by equation (18) or equation (21).

The difference between the formulæ for dispersion derived here and those of the Debye theory are best seen by comparing the expressions which they yield for the molar polarization. On the Debye Theory:

$$\frac{M}{\rho} \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{3} \left[ \alpha_0 + \frac{\mu^2}{3kT} \left( \frac{1}{1 + i\omega\tau'} \right) \right].$$

<sup>18</sup> After a suggestion made by E. T. Hoch, *B. S. T. J.*, November (1922), and by H. H. Race, *Jour. A. I. E. E.*, 51, 354 (1932).

The present derivation gives:

$$\frac{M}{\rho} \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{3} \left[ \frac{k_i}{L} + \frac{ne^2}{fL} \left( \frac{1}{1 + i\omega\tau'} \right) \right].$$

The constant  $\alpha_0$  has the same significance as  $k_i/L$ , only the notation being different; both represent the optical frequency, or "instantaneous," polarizability;  $\mu$  is the permanent electric moment of the molecule,  $k$  Boltzmann's constant and  $T$  the absolute temperature. The quantity  $ne^2/fL$  which corresponds to  $\mu^2/3kT$  in the Debye formula contains three constants  $n$ ,  $e$ , and  $f$  whose physical significance is indicated only in a general way (see Appendix).  $\tau'$  (or in Debye's notation  $\tau$ ) is equal to  $4\pi\eta a^3/kT$  in the Debye theory while in the formula derived here  $\tau' = r/f$  where  $r$  is a frictional coefficient whose physical origin is not specified. Thus though the formula for molar polarization derived here is not directly useful as a means of investigating the molecular (or other) origin of dielectric polarizations, it facilitates distinguishing those aspects of the Debye formula which are peculiar to a polarization depending upon changes in the orientation of polar molecules which are free to assume any (or at least more than one) orientation from the more general aspects shared by other types of polarization, such as the one specified by (18) and (21). Thus, the functions  $\mu^2/3kT$  and  $4\pi\eta a^3/kT$  are peculiar to the Debye theory, while the function  $(1 + i\omega\tau)^{-1}$  also appears in the dispersion formula derived here, as well as in other formulæ to be discussed below.

We have seen that the viscous-elastic type of polarization specified by (18) and (21) produces a complex dielectric constant given by (39), or by the equivalent equations (41), (41a), (41b), where

$$\tau = \frac{\tau'(\epsilon_0 + 2)}{(\epsilon_\infty + 2)},$$

and that the same formulæ express the complex dielectric constant on the Debye theory of polar molecules when the constants  $\tau'$  and  $\epsilon_0 - \epsilon_\infty$  (or  $k_0 - k_\infty$ ), are given the values derived for them on the Debye theory. Other theories have been proposed to explain the variation of dielectric constant and dielectric loss with frequency, but for the most part these have been derived for composite dielectrics, consisting of two or more layers of different materials, or of small spheres of one material dispersed or embedded in another material. These theories also yield formulæ (41), (41a) and (41b) for the complex dielectric constant, the expressions for  $\tau'$  and  $\epsilon_0 - \epsilon_\infty$  being, of course,



different from those of the Debye theory.<sup>19</sup> These expressions are included in Table I.

TABLE I  
CONSTANTS OF THE FORMULA FOR THE COMPLEX DIELECTRIC CONSTANT  
EQUATIONS (41), (41a) AND (41b)

Type of Polarization	$\epsilon_0 - \epsilon_\infty$	$\tau$	$k = f(\epsilon)$
1. Orientation of polar molecules (The Debye theory). <sup>1</sup>	$\frac{4\pi}{3} \cdot \frac{(\epsilon_0+2)(\epsilon_\infty+2)}{3} \cdot \frac{L\mu^2}{3kT}$	$\frac{(\epsilon_0+2)}{(\epsilon_\infty+2)} \cdot \frac{4\pi\eta a^3}{kT}$	Eq. (5)
	$\frac{4\pi}{3} \cdot \frac{L\mu^2}{3kT}$	$\frac{4\pi\eta a^3}{kT}$	Eq. (6)
	$\frac{34\pi}{3} \cdot \frac{L\mu^2}{3kT}$	$\frac{4\pi\eta a^3}{kT}$	Eq. (9)
2. Displacement of charged particles against elastic restoring forces and viscous frictional forces of undetermined origin, as specified in equation (17). (Modification of Drude theory). <sup>2</sup>	$\frac{4\pi}{3} \cdot \frac{(\epsilon_0+2)(\epsilon_\infty+2)}{3} \cdot \frac{ne^2}{f}$	$\frac{\epsilon_0+2}{\epsilon_\infty+2} \cdot \frac{r}{f}$	Eq. (5)
	$4\pi \cdot \frac{ne^2}{f}$	$\frac{r}{f}$	Eq. (6)
	$\frac{34\pi}{3} \cdot \frac{ne^2}{f}$	$\frac{r}{f}$	Eq. (9)
3. Interfacial or ionic polarizations:			
(a) Two-layer dielectric; layer ( $\epsilon_1, \gamma_1$ ) being of same thickness as layer ( $\epsilon_2, \gamma_2$ ), (Wagner). <sup>3</sup>	$\frac{(\epsilon_1\gamma_2 - \epsilon_2\gamma_1)^2}{(\epsilon_1 + \epsilon_2)(\gamma_1 + \gamma_2)^2}$	$\frac{\epsilon_1 + \epsilon_2}{\gamma_1 + \gamma_2}$	
(b) Special case of (a); high-resistance blocking layer at electrode/dielectric boundary (Joffé). <sup>4</sup>	$C_1/C_\infty$	$RC_1$	
(c) Suspension of spheres ( $\epsilon_1, \gamma_1$ ) in a medium ( $\epsilon_2, \gamma_2$ ), where $p \ll 1$ (Wagner). <sup>6</sup> (Gemant). <sup>7</sup>	$\frac{9p(\epsilon_1\gamma_2 - \epsilon_2\gamma_1)^2}{(2\epsilon_2 + \epsilon_1)(2\gamma_2 + \gamma_1)^2}$	$\frac{2\epsilon_2 + \epsilon_1}{2\gamma_2 + \gamma_1}$	
(d) Special case of (c); conducting spheres in an insulating medium, where $\epsilon_1 = \epsilon_2$ and $\gamma_2 \ll \gamma_1$ (Wagner). <sup>5</sup>	$3p\epsilon_1$	$3\epsilon_1/\gamma_1$	
(e) Special case of (d); conducting shells (Miles and Robertson). <sup>6</sup>	$3p\epsilon_1$	$\frac{3\epsilon_1 b}{2\gamma_2 d}$	

<sup>1</sup> Reference numbers in this table refer to list of references at the end of this paper.

Table I contains a list of expressions which, when substituted for  $(\epsilon_0 - \epsilon_\infty)$  and  $\tau$  in (41a) and (41b), give several formulæ for the complex dielectric constant. Included in this list are most of the formulæ which have been proposed to explain the simplest type of variation of

<sup>19</sup> Cf. Gemant, "Elektrophysik der Isolierstoffe," Berlin (1930).

dielectric constant and loss factor with frequency which is observed in the different classes of materials to which the various items in the table refer. In some cases the original formulæ, as they appear in the literature, have been expressed in terms which do not show an obvious equivalence to (41), (41a) and (41b), but by re-expressing them in the form (41) and then determining  $\epsilon_0$  and  $\epsilon_\infty$  by letting  $\omega = 0$  and  $\infty$ , respectively, the list of expressions given in Table I is obtained. It is interesting that theories based on such widely dissimilar physical mechanisms as rotating polar molecules (Item 1, Table I) and a blocking-layer of high resistance at an electrode/dielectric interface (Item 3(b), Table I) should yield an identical form of variation with frequency.

For the first two polarizations listed in Table I, the alternative expressions obtained by assuming three alternative relationships between polarizability and dielectric constant are given. By means of Table II the quantities  $(k_0 - k_\infty)$  and  $\tau'$  can be obtained from  $(\epsilon_0 - \epsilon_\infty)$

TABLE II

THE RELATIONSHIP BETWEEN  $(k_0 - k_\infty)$  AND  $(\epsilon_0 - \epsilon_\infty)$  AND BETWEEN  $\tau'$  AND  $\tau$

	$(k_0 - k_\infty)$	$\tau'$
Clausius-Mosotti Relation.....	$\frac{3}{4\pi} \cdot \frac{3(\epsilon_0 - \epsilon_\infty)}{(\epsilon_0 + 2)(\epsilon_\infty + 2)}$	$\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \tau$
Gases.....	$\frac{1}{4\pi} \cdot (\epsilon_0 - \epsilon_\infty)$	$\tau$
Wyman's Empirical Relation .....	$\frac{3}{4\pi} \cdot \frac{\epsilon_0 - \epsilon_\infty}{8.5}$	$\tau$

and  $\tau$  in Table I. The resulting expressions can then be substituted for  $(k_0 - k_\infty)$  and  $\tau'$  in equation (26) yielding expressions for the polarizabilities of the different types of polarization listed in Table I. The molar polarization can then be obtained by multiplying (26) by  $(4\pi/3)(M/\rho)$ . However, in general it is not likely that any useful purpose is to be served by calculating the molar polarization for interfacial polarizations; a more significant quantity would be the polarization per conducting particle, when the polarization is of the type (3d), Table I, and the number of conducting particles per unit volume can be estimated.

We have pointed out that a number of theories which have been proposed for the explanation of the variation of dielectric constant with frequency may be expressed in the forms (41a) and (41b) when the expressions listed in Table I are substituted for  $(\epsilon_0 - \epsilon_\infty)$  and  $\tau$ , but we have not yet indicated how these formulæ agree with experimental data. For such materials as ice (see Fig. 3, for example) and for

certain alcohols and glycols, the experimental points agree fairly closely with the curves obtained by plotting equations (41a) and (41b) for a suitable choice of the values of the constants.

But for many other dielectrics, particularly non-homogeneous systems or disperse systems such as those listed under Item 3, Table I, the simple dispersion formulæ (41a) and (41b) often fall very far short of adequately representing the experimental data. Von Schweidler<sup>20</sup> and Wagner<sup>21</sup> have attempted to explain the form of dispersion curves obtained for such materials by postulating that the polarizations

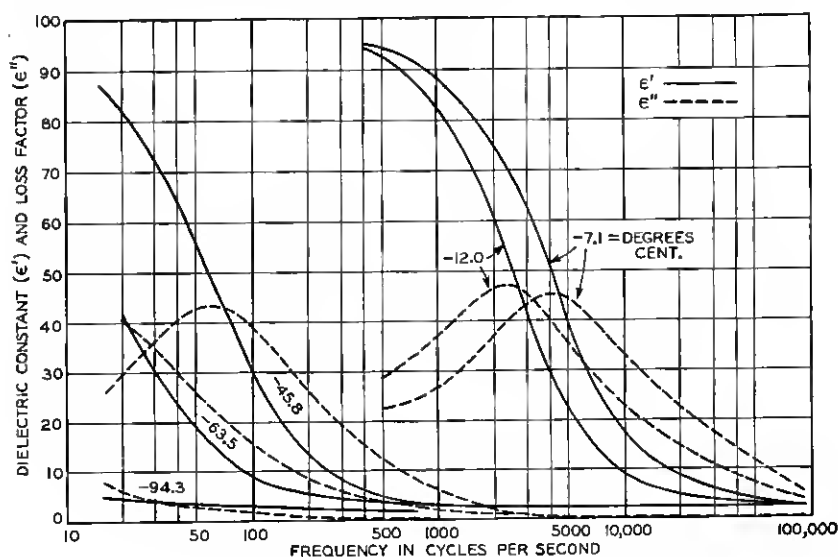


Fig. 3—Experimental dispersion curves for ice.

induced in the dielectric have a wide range of relaxation times at any given temperature, instead of a single relaxation time, as for the polarizations listed in Table I. A further contribution to the theory of the distribution of relaxation times has recently been made by Yager.<sup>22</sup> However, in spite of the existence of many materials which do not show the type of dispersion described by (41a) and (41b), the value of these formulæ in interpreting experimental data is considerable, particularly as applied to pure materials.

Table I emphasizes the point that mere agreement of experimental data for dielectric constant and dielectric loss with the theoretical

<sup>20</sup> E. v. Schweidler, *Ann. d. Phys.*, (4) (24), 711 (1907).

<sup>21</sup> K. W. Wagner, *Archiv f. Elektrotechnik*, 2, 371 (1914).

<sup>22</sup> W. A. Yager, *Physics*, 7, 434 (1936).

curves obtained by plotting (41a) and (41b) for suitably adjusted values of the constants only places the type of mechanism to which the observed dispersion can be attributed within the rather large category which includes at least the seven types of mechanism listed in the table. Data showing the dependence of  $(k_0 - k_\infty)/\rho$  on temperature allows a further specialization of the processes which could account for the observed behavior; and of course a number of possibilities can be discarded on general grounds of physical improbability. And finally, agreement of the constants calculated from dielectric measurements with the values calculated from independent estimates of the sizes and other characteristics of the molecules or other elementary units which contribute to the polarization provides the most convincing evidence of the nature of the polarization. Such agreement is frequently obtained in the application of the Debye theory to gases and liquids.

The characteristics which can be deduced from equations (41a) and (41b) without substituting for the constants theoretical expressions, such as those given in Table I, are of considerable value in interpreting electrical measurements upon dielectrics. It may be convenient to describe these as the *general* characteristics of anomalous dispersion, distinguishing them thereby from the *special* characteristics peculiar to particular kinds of dielectric polarization which share the property of producing anomalous dispersion in the radio and power range of frequencies.

#### APPENDIX

The following list contains the definitions of the quantities which appear in Table I:

- $\epsilon_1, \epsilon_2, \gamma_1, \gamma_2$  are respectively the dielectric constants and conductivities of two materials designated by subscripts 1 and 2, the unit of conductivity being such that  $\gamma = 36\pi \times 10^{11} \lambda$ , where  $\lambda$  is in  $(\text{ohm} \cdot \text{cm})^{-1}$ .
- $\epsilon_0, \epsilon_\infty$  are respectively the dielectric constant at the lower and upper extremities of dispersion curves; they are called the zero-frequency (or static) dielectric constant and the infinite-frequency dielectric constant,
- $L$  is the number of molecules per unit volume,
- $\eta$  the viscosity of a liquid containing polar molecules,
- $k$  Boltzmann's constant,
- $T$  the absolute temperature,
- $\mu$  the permanent electric moment of a polar molecule,

- $a$  the radius of a polar molecule, assumed to be spherical,
- $b$  the radius of a colloidal particle,
- $d$  the thickness of a conducting skin on the particle of radius  $b$ ,
- $r$  a frictional resistance coefficient of unspecified origin,
- $f$  an elastic restoring force coefficient of unspecified origin,
- $n$  the number per unit volume of elementary charged particles subject to certain specified conditions,
- $p$  the ratio of the volume occupied by the spherical particles in  $(3c, d, e)$  to the total volume,
- $C_1$  the capacity of the blocking layer of  $(3b)$ , Table I,
- $R$  the resistance of the dielectric, exclusive of the blocking layer.

The following list contains the definitions of quantities which appear in other parts of the article.

- $\omega$  is  $2\pi$  times the frequency of alternation of the applied field,
- $V$  the applied voltage,
- $E$  the intensity of the applied field,
- $P$  the polarization per unit volume induced by a field  $E$ ,
- $F$  the internal or local field,
- $\rho$  the density of the dielectric,
- $M$  the molecular weight of the material of which the dielectric is composed,
- $m$  the mass of a molecule; in another context, the mass of any charged particle considered in the discussion,
- $N$  is Avogadro's number,  $6.06 \times 10^{23}$  molecules per mole,
- $s$  the displacement of a charged particle from an equilibrium position by an applied field,
- $\dot{s}$  the velocity of the charged particle in the applied field,
- $\ddot{s}$  the acceleration of the particle in the applied field.

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